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# Manipulation of charge carrier injection into organic field-effect transistors by self-assembled monolayers of alkanethiols†

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Charge carrier injection into two semiconducting polymers is investigated in field-effect transistors using gold source and drain electrodes that are modified by self-assembled monolayers of alkanethiols and perfluorinated alkanethiols. The presence of an interfacial dipole associated with the molecular monolayer at the metal/semiconductor interface changes the work function of the electrodes, and, hence, the injection of the charge carriers. The FET characteristics are analysed with the transfer line method and the hole injection into poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and regio-regular poly(3-hexyl)thiophene (rr-P3HT) is investigated. The device parameters are corrected for the contact resistances of the electrodes and the mobilities of the polymers (MEH-PPV,  $\mu_{\text{FET}} = 4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and rr-P3HT,  $\mu_{\text{FET}} = (1-2) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) are determined. The contact resistance obtained for the SAM-modified electrodes is at least one order of magnitude larger than for untreated contacts.

## Introduction

Organic field-effect transistors (OFETs), being promising candidates for low-cost, low speed and large-area display applications, have gone through extensive improvements in recent years.<sup>1</sup> Although organic (opto)electronic devices are at the edge of commercialization there are still fundamental challenges concerning the formation of contacts, charge injection from the contacts and transport of the injected charges through the device.<sup>2-4</sup> These are key parameters for reliable operation of an organic (opto)electronic device. Charge injection into the device is efficiently achieved *via* Ohmic contacts by choosing a metal with a work function that matches the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) of the organic semiconductor (within a few tenths of an electronvolt), respectively. In general, however, there is a misalignment between the energy levels of the contacts and the semiconducting polymer and therefore a barrier exists for injection of the charges from the metal into the polymer. Consequently, the performance of OFETs can be severely affected by this injection barrier. Thus manipulation of the injection barrier at the metal/polymer interface is of interest. Changing the injection barrier will result in either facilitating charge injection and therefore improving the performance of the device or reducing the charge injection and degrading the performance.<sup>5,6</sup> Engineering of the injection barrier is achieved either through manipulation of the HOMO (or the LUMO) of the polymer, or by modifying the work function of the

electrodes. The latter approach is realized by insertion of polar molecules at the metal/(semiconducting) polymer interface. This can be regarded as inserting a sheet of electric dipoles at the interface which in turn results in a charge redistribution on the metal surface. From classical electrostatics one can calculate the potential drop caused by this dipole sheet. Imposing a sheet of dipoles on metals can be done by molecules that are evaporated<sup>7</sup> on the electrodes or molecules that are adsorbed, physically or chemically, on the surface. A prime example of the latter is a self-assembled monolayer (SAM) that consists of chemisorbed thiols on gold.<sup>8-11</sup> Alternatively, one can regard the work function of a metal as a measure of the extension of the wave function of the free electrons at the surface of the metal into vacuum. Exposing the metal to an electric field caused by the dipolar monomolecular layer results in a larger extension of the wave function of the free electron into the vacuum and, hence, the electron is easier to extract from the metal and the work function of the metal is reduced.

Alkanethiols are well known to self-assemble in a uniform and densely packed monolayer on metal surfaces like gold.<sup>10</sup> The presence of electric dipoles associated with the molecule and the gold-sulfur bond, at the metal/molecule interface, will result in a modification of the work function of gold (or metals in general).<sup>11</sup> Thiol-based SAMs have been used to modify the OFET characteristics of sexithiophene and pentacene as the semiconductor.<sup>5,12</sup> However, changes in interface morphology of such crystalline materials cannot be excluded. Recently, we have demonstrated the successful utilization of alkanethiols to tune the work function of gold and silver electrodes and observed improvement of the charge injection and blocking in organic light-emitting diodes and photovoltaic cells.<sup>13</sup> By using alkanethiols or perfluorinated alkanethiols on silver, the current density was modified by 6 orders of magnitude. Hamadani *et al.* applied conjugated thiols in a bottom contact geometry in OFETs to control the charge injection

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into regio-regular poly(3-hexyl)thiophene (rr-P3HT).<sup>14</sup> Besides using the SAMs for tuning the charge injection in (opto)-electronic devices, it is demonstrated that the interfacial layers formed by a SAM of hexamethyldisilazene (HMDS) on silicon oxide at the insulator/semiconductor interface of an OFET improves the wetting of the rr-P3HT solution on the surface and the mobility of the charge carriers is increased due to morphological changes.<sup>15</sup>

Here we demonstrate the tuning of the work function of the gold electrodes from 5.6 eV to 4.0 eV with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) and hexadecanethiol (HDT), respectively, and utilize this technique to manipulate charge injection in organic field-effect transistors. The low work function electrodes (modified with hexadecanethiol) give rise to an injection barrier for holes, resulting in a larger threshold voltage and a suppression of the current in the OFETs. In contrast, the addition of the perfluorinated SAM to the gold electrodes increases the work function. Since gold creates already a nearly Ohmic contact with poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV, HOMO at 5.2 eV) and regio-regular poly(3-hexyl)thiophene (rr-P3HT, HOMO at 4.8 eV), devices modified with the perfluorinated SAM, which increase the work function to 5.6 eV, do not show significantly improved behavior. Finally, the thermal stability of the SAM is also investigated to elucidate the influence of annealing on the interfacial issues of the OFET.

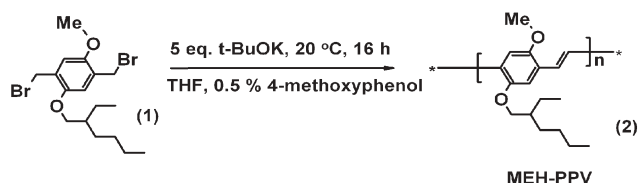
## Experimental

### Hexadecanethiol and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol

Hexadecanethiol (CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>-SH) (Aldrich) was distilled prior to use. Perfluorinated decanethiol (CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>(CH<sub>2</sub>)<sub>2</sub>-SH) was synthesized according to reference 16. These compounds are readily obtained in high yields.

### MEH-PPV

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was synthesized *via* the Gilch method, Fig. 1.<sup>17</sup> In a three necked round-bottom flask, well flushed with N<sub>2</sub> and equipped with a mechanical stirrer, were dissolved 2.24 g (20 mmol) of *t*-BuOK and 2.5 mg (0.02 mmol) of 4-methoxyphenol in 100 ml of dried THF. A solution of 2.11 g (5.0 mmol) of 1,4-bis(bromomethyl)-2-methoxy-5-(2'-ethyl hexyloxybenzene) (**1**) in THF (15 ml) was then added in 0.5 hour with a dropping funnel. After 16 h the viscous solution was precipitated into methanol (1 l). The resulting polymer was collected by filtration and washed thoroughly with methanol.



**Fig. 1** Synthesis of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) *via* the Gilch route.

The polymer is further purified by dissolving in 120 ml of chloroform and reprecipitation in acetone (1 l)

### rr-P3HT

Regioregular poly(3-hexylthiophene) (rr-P3HT, electronic grade; 98.5% regioregular; Rieke Metals, Inc.) was dissolved in distilled toluene, dedoped with hydrazine at 60 °C and precipitated in methanol. The fraction collected was Soxhlet extracted for at least 64 h with methanol, *n*-hexane, CH<sub>2</sub>Cl<sub>2</sub> and finally with CHCl<sub>3</sub>. The chloroform fraction was precipitated in methanol, dried under vacuum and stored in the glove box under N<sub>2</sub> atmosphere.

### Self-assembled monolayer formation on FET substrates

Prior to use, the FET substrates were rinsed thoroughly with acetone and 2-propanol, and blown dry with deionized N<sub>2</sub>. The self-assembling molecules were dissolved in ethanol ( $\sim (1-3) \times 10^{-3}$  M). The FET substrates with gold electrodes were immersed into the solution for at least 2 days. After the self-assembly process, the substrates were thoroughly rinsed with ethanol, toluene, and 2-propanol, dried with a deionized N<sub>2</sub> flow, and used immediately for spin coating of the organic semiconductor.

### Work function measurements

The Kelvin probe was calibrated with freshly cleaved highly oriented pyrolytic graphite (HOPG) under nitrogen atmosphere (glove box). Freshly cleaved HOPG is known to have a stable work function of 4.48 eV.<sup>13</sup> Gold substrates were prepared by thermal evaporation of 150 nm of Au on SiO<sub>2</sub> substrate with 1 nm of chromium as adhesion layer. The samples were UV-ozone cleaned for five minutes and immediately immersed in the solution containing the thiols. HDT solutions were prepared with concentrations of  $1 \times 10^{-5}$  M and  $\sim 3 \times 10^{-3}$  M. The immersion time was varied from one minute to several days. The substrates were rinsed as described for FETs and the work function was measured in a glove box by a Kelvin probe. For probing the thermal stability of SAMs, the substrates were first immersed in  $\sim (1-3) \times 10^{-3}$  M solution over night. After rinsing the substrates with ethanol, toluene and 2-propanol and drying with a deionized N<sub>2</sub> flow, SAM functionalized substrates were coated with a polymer layer by spin coating of polystyrene from a 5 mg ml<sup>-1</sup> solution in toluene. The samples (Au/SAM/PS) were annealed on a calibrated hotplate in the glove box for two hours at different temperatures. After cooling to room temperature the polystyrene layer was removed with acetone and the substrate was rinsed with ethanol, toluene and 2-propanol, and dried with a deionized N<sub>2</sub> flow. Finally, the work function was measured in the glove box.

### Devices and electrical measurements

FETs were made using heavily doped silicon wafers as gate electrode, with a 200 nm thick layer of thermally grown SiO<sub>2</sub> as gate dielectric. By conventional photolithography, gold drain and source electrodes were patterned on top of the SiO<sub>2</sub>. Modification of the substrate surface prior to the deposition of

the organic active layer made the substrate flat and influenced the film morphology.<sup>15</sup> A 10 nm thick layer of titanium was used as adhesion layer for the gold on silicon oxide. In our experiments, the device was then treated with the primer HMDS in order to make the surface hydrophobic.<sup>18</sup> The device was finished by spin-coating the organic active layer from solution. The layer thickness was typically 200 nm. The solvents used were toluene and chloroform for MEH-PPV and rr-P3HT, respectively. In order to avoid contamination with water and oxygen, the polymers were spun in the glove box and then transported directly to the measurement setup. Two FET configurations, Fig. 2, were used: finger configuration with typical length  $L = 10\ \mu\text{m}$  and width  $W = 10000\ \mu\text{m}$ ; ring configuration with  $L = 10\text{--}40\ \mu\text{m}$  and  $W = 1000\ \mu\text{m}$ . For both transistors the capacitance of the gate insulator is  $17\ \text{nF cm}^{-2}$ . The ring configuration was used in order to minimize contributions by parasitic currents. Electrical measurements were carried out in a probe station under high vacuum ( $10^{-6}$  mbar) with a Keithley 4200 semiconductor analyzer.

## Results and discussion

### Modifying the work function: magnitude and (thermal) stability

We examined the effect of the PFDT and HDT SAMs on the work function of Au. A complete monolayer of PFDT and HDT increases the work function to 5.6 eV and decreases the work function of Au to 4.0 eV, respectively (Fig. 3).<sup>13</sup> Both the magnitude and the stability of the work function of the SAM-modified Au electrode are of great concern. A highly stable (tuned) work function in time is desired when applications are envisioned that use these molecular layers in electronic devices.

To address the magnitude, a series of experiments with diluted SAM solutions were conducted with different immersion times. The results presented in Fig. 3 indicate that the process of the monolayer formation is indeed very fast and even after reducing the concentration of the solution by a factor of 100, the shift in the work function approaches its maximum value after 100 minutes in solution. Reducing the concentration of the solution provides the possibility of tuning the work function of Au to preselected values by immersing the substrate for a short time in the solution. The explanation lies in the nature of the self-assembly process, since the monolayer does not fully cover the Au surface during short immersion time<sup>19</sup> and, therefore, the resulting work function is less than expected. Utilizing different immersion times of the Au-coated substrate in a  $1 \times 10^{-5}$  M solution of HDT, the work function of Au can be tuned between 4.5 and 4.0 eV.

The utilization of SAMs in devices also requires a good stability of the SAM over longer periods of time. The stability measurements of the modified substrates, shown in the inset of

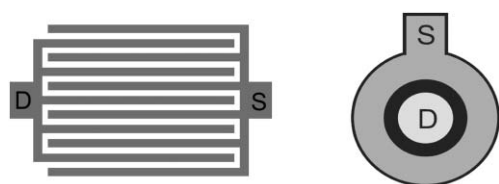


Fig. 2 Finger (left) and ring (right) geometries of FETs.

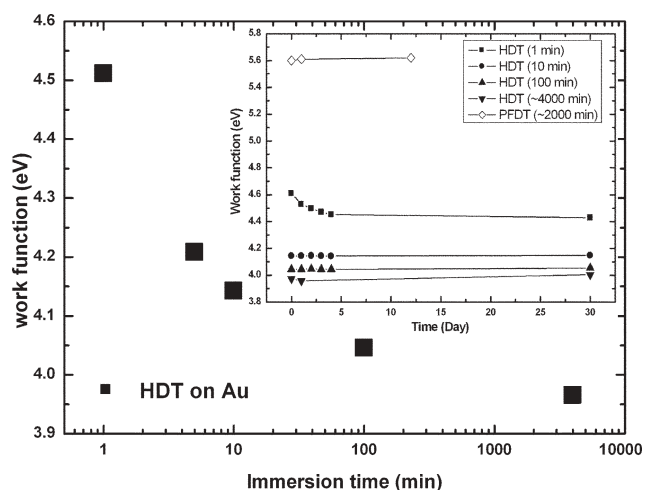
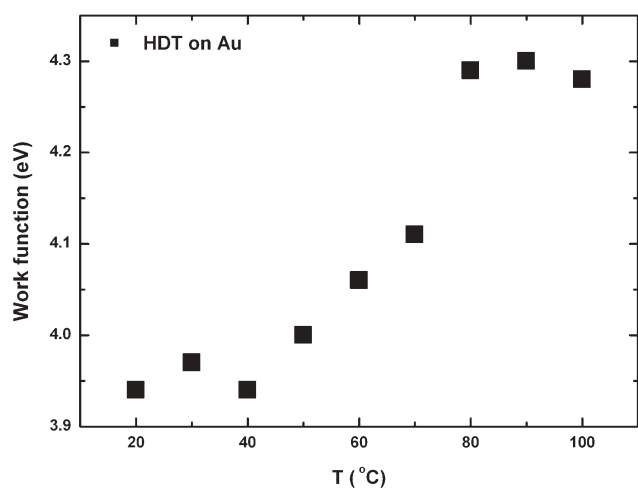


Fig. 3 The work function measured with the Kelvin probe as function of the immersion time of the Au-coated substrate in the hexadecane thiol SAM solution of  $1 \times 10^{-5}$  M. Inset: The stability of the work function for PFDT and for HDT (for different immersion times).

Fig. 3, clearly indicate that both monolayers (HDT and PFDT) are very stable when kept in  $\text{N}_2$  atmosphere at room temperature and no degradation of the modified electrodes and their work functions is observed after 1 month.

To improve the performance of polymer-based FETs, post-production treatments such as annealing of the polymer are often required to improve the properties of the polymer and/or the physical contacts between the polymers and the electrodes. SAMs are known to be less thermally stable<sup>20</sup> and, therefore, the thermal stability of the SAMs used is investigated in a configuration that mimics the actual device. To investigate the work function of SAM-modified Au electrode with the Kelvin probe at elevated temperatures, we conducted a series of experiment with large gold-coated glass substrates ( $3 \times 3\ \text{cm}$ ) on which a SAM was applied and covered the SAM with a layer of polystyrene (PS), as described in the Experimental section. After thermal annealing the Au/SAM/PS stack for 2 h on a hot plate in the glove box, the PS was removed by thoroughly rinsing with solvents, and the work function of the remaining Au/SAM was measured with the Kelvin probe (Fig. 4). As the annealing temperature is increased, the work function increases steadily, and around  $80\ ^\circ\text{C}$  a total shift of 0.4 eV is observed. This higher work function indicates less dipoles on the Au surface and, thus, a lower grafting density of the SAM on Au upon annealing. A decreasing grafting density can be correlated to phase transitions of the 2D packing of the SAM as was observed by Qian *et al.*<sup>20</sup> These authors demonstrate the appearance of low density phases upon annealing above  $70\ ^\circ\text{C}$  due to desorption of alkanethiol molecules from the Au surface. Obviously, a lower packing density of the dipoles on the Au surface results in a smaller potential shift of the work function of the annealed substrates. We note that in our experiments the SAM cannot freely desorb from the surface since we have spin coated a PS layer onto the SAM. Therefore, the alkanethiols have to diffuse into the PS layer which is very likely at annealing temperatures above





**Fig. 4** Stability of the HDT-modified Au substrates expressed by plotting the work function as measured with the Kelvin probe *versus* temperature.

70–80 °C (even though the glass transition temperature of PS is  $\sim 100$  °C). Thus annealing polymer-based electronic devices with SAM-modified electrodes at temperatures above  $\sim 60$  °C can enhance the morphology of the polymer and its electronic properties, but will result in a reduced work function shift even if the monolayer is covered with a thin polymeric film. Both contrasting effects should be taken into account when electrical device parameters are extracted from such annealed field-effect devices.

### Manipulation of charge injection in OFETs

Previously, we reported on the use of SAMs to tune the work functions of metal electrodes (Au, Ag) in organic electronic devices such as polymer (light-emitting) diodes and photovoltaic cells.<sup>13</sup> For these diode geometries the effect of the electrode modification is obvious: one can block the injection of holes or electrons. In three terminal devices, this effect is less clear since high gating potentials result in a highly electrostatically doped semiconductor, which can give rise to strong band bending at the drain electrode/polymer interface. To evaluate the influence of the work function shift on the characteristics of the devices, a series of transistors were processed in which the gold electrodes were functionalized with two different SAMs with opposing dipole moments. Furthermore, two different semiconducting polymers (MEH-PPV and rr-P3HT) were used in these SAM-modified FETs. Measurements were performed according to the procedures described in the Experimental section.

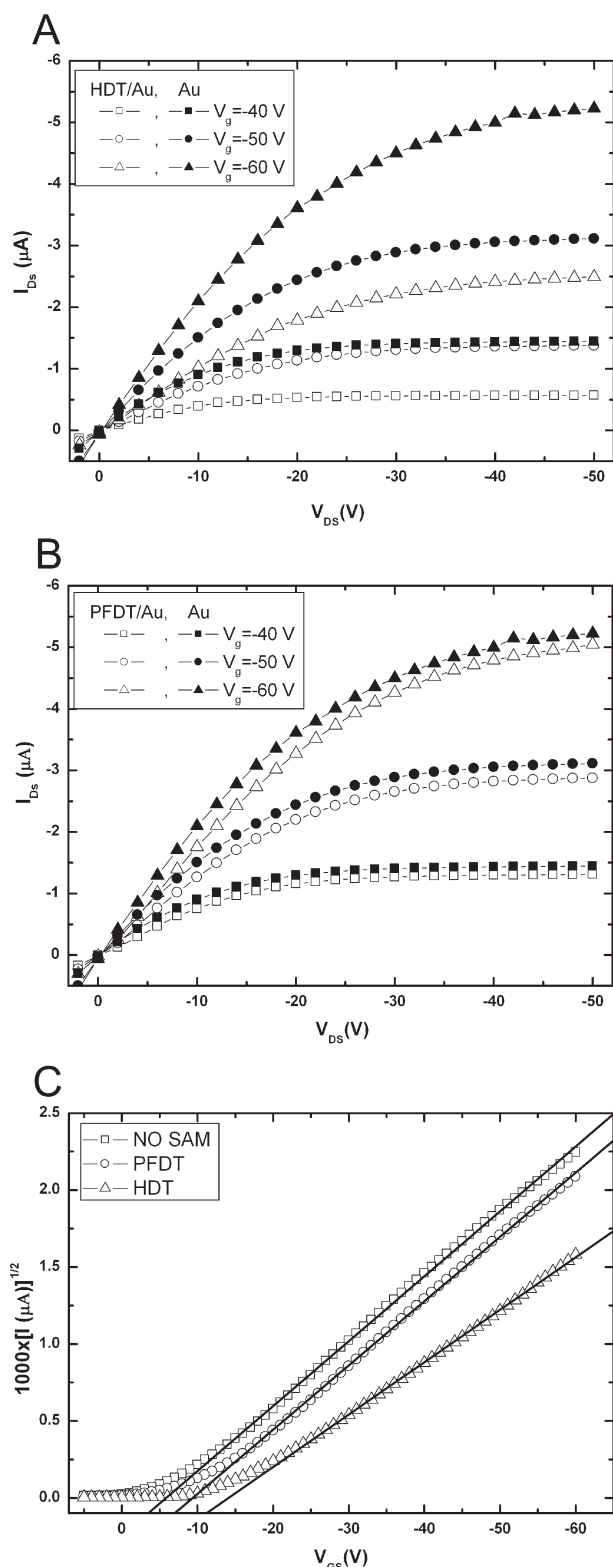
### Hole injection in MEH-PPV

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) has its HOMO centered at 5.2 eV. Therefore a negligibly small injection barrier with gold is obtained, since the work function of vapor-deposited Au is  $\sim 4.9$  eV (as measured with the Kelvin probe). The MEH-PPV/Au contact can be considered an Ohmic contact. Modifying the contacts with the HDT results in a work function of 4.0 eV and creates

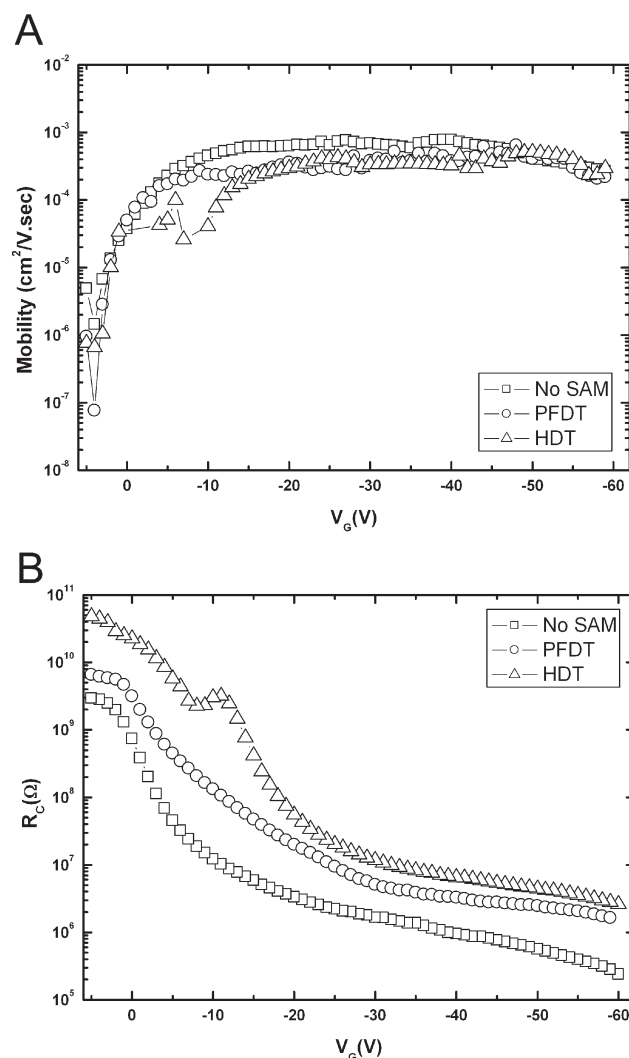
a large injection barrier of  $\sim 1$  eV for the injection of holes. On the other hand, PFDT increases the work function of gold to 5.6 eV. In the latter case an Ohmic contact is expected.

Output characteristics of the two sets of finger transistors with  $W/L = 10000(\mu\text{m})/20(\mu\text{m})$  are shown in Fig. 5 and demonstrate the effect of different SAMs on the charge injection. The results show that HDT suppresses the current (both in linear and saturation regimes) of the transistor, while in the case of PFDT the output characteristics are almost unaffected compared to the untreated transistor. As expected, PFDT-modified Au contacts form an Ohmic contact with MEH-PPV similar to untreated Au contacts. The small difference in the current between the PFDT treated and untreated transistor can be explained by the presence of the molecular monolayer at the metal/semiconductor interface, which can be regarded as a tunnel barrier at the interface that introduces an additional resistance at this interface.

The FET characteristics of MEH-PPV with the HDT-modified Au electrodes demonstrate clearly that the large hole injection barrier suppresses the charge injection in these FETs. By investigating the transfer characteristics in the saturation regime, we derive the threshold voltage from the intercept of the linear fit. From the slope, the mobility can be extracted.<sup>1</sup> As expected, both the untreated Au and Au modified with PFDT create an Ohmic contact, and, consequently, the slopes of the linear fits are similar, which implies similar apparent mobilities. Although the threshold voltage is mostly dominated by the properties of the gate dielectric and the dielectric/polymer interface, we observe a small dependence on the electrodes.<sup>21</sup> Further analysis of the transfer data in Fig. 5(c) shows that the mobilities obtained for untreated and for the PFDT-modified transistors are different than the mobility extracted for the HDT-modified transistor (slope of the linear fit). From this analysis, one may deduce that the SAM affects the mobility of charge carriers in MEH-PPV. Since MEH-PPV is an amorphous material, its charge transport is isotropic and governed by the concentration of charge carriers.<sup>3,22</sup> Furthermore, the mobility is an intrinsic property of the material which is dependent on the charge carrier density<sup>3,22</sup> and independent of the geometry and the contacts. Therefore, the mobility analysis mentioned above is not applicable for the SAM-modified transistors since the contacts of the transistors are playing a role in the charge injection process. A more correct method to extract mobilities from the data obtained is to perform an analysis using the transfer line method (TLM).<sup>12,14,23</sup> This method relies on measuring a series of transistors with the same channel width and different channel lengths. Via data analysis of the transfer characteristics, one can correct for the contact resistance and evaluate the true mobility of the organic semiconductor. Therefore, a series of finger transistors with channel lengths of 7.5, 10, 15, 20, 30 and 40  $\mu\text{m}$  and channel width of 10000  $\mu\text{m}$  were measured and the TLM method was applied. These measurements were repeated for FETs with their Au contacts modified with HDT and PFDT. The analysis resulted in the same mobility for both SAM-modified and untreated FETs of  $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for MEH-PPV at low  $V_{\text{DS}}$  ( $V_{\text{DS}} = -2$  V) and high  $V_{\text{G}}$  (where DS means drain-source and G means gate). Fig. 6 shows the calculated mobility and contact resistance of the transistors



**Fig. 5** Output characteristics of a FET based on MEH-PPV with (a) untreated Au electrodes and HDT-modified electrodes and (b) untreated Au electrodes and PFDT-modified Au electrodes, and (c) the transfer characteristics in the saturation regime and the increase of the threshold voltage for SAM-modified Au electrodes in MEH-PPV-based transistors.



**Fig. 6** TLM analysis of the MEH-PPV-based transistors at  $V_{DS} = -2$  V: (a) mobility and (b) contact resistance of the untreated, and PFDT- and HDT-modified Au electrodes in OFETs.

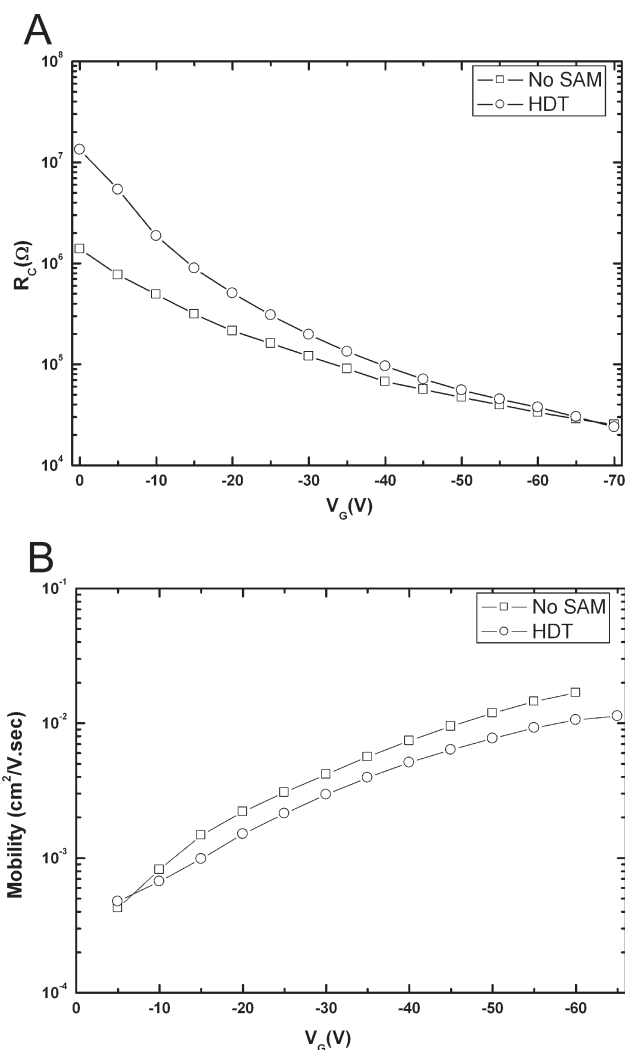
versus  $V_G$ . Fig. 6(a) demonstrates that the mobility is an intrinsic material property and therefore independent of the contact modification. In this respect TLM is a good method to overcome the obstacles associated with the conventional analysis for OFETs at linear and saturation regimes (Fig. 5(c)).

Furthermore, the analysis for the contact resistances of the HDT-modified, PFDT-modified and untreated FET demonstrates an increasing contact resistance with the length of the SAM (Fig. 6(b)). The difference in the output characteristics of the transistors as demonstrated in Fig. 5(b) is well supported by TLM. HDT raises the contact resistance in the low gate voltage regime by more than two orders of magnitude compared to the untreated Au contacts. PFDT on the other increases the contact resistance by less than one order of magnitude. In general, the contact resistances decrease when the gate voltage is increased. For large contact resistances (larger than the bulk resistance of the semiconducting polymer in the transistor channel) most of the applied source-drain potential drops across the contacts instead of the channel.

Therefore, the current that is extracted from the transistor decreases.

### Hole injection in rr-P3HT

Regio-regular P3HT has been the subject of many studies in OFETs. Due to the presence of highly ordered crystalline phases at the semiconductor/dielectric interface, a higher mobility is obtained compared to other semiconducting polymers such as MEH-PPV. The on/off ratio of the transistor is increased upon annealing due to dedoping of the rr-P3HT.<sup>24</sup> In the case of using SAM-modified electrodes, one has to be careful using thermal treatment of the transistors since SAMs of alkanethiols, as shown in Fig. 4, are thermally unstable at temperatures above 60 °C.<sup>20</sup> Therefore, we infer that annealing of rr-P3HT is unsuitable for experiments in which the Au electrodes are modified with SAMs of alkanethiols. Consequently, we conducted all the experiments with rr-P3HT at room temperature without any thermal treatment. Annealing of OFETs with rr-P3HT and SAM-modified Au electrodes<sup>14</sup> will also influence the anisotropic nature of the charge transport in rr-P3HT. Furthermore, a change of the interfacial morphology that P3HT adopts at the interface with the SAM has an impact on the mobility of the material and performance of the device.<sup>25</sup> The presence of a perfluorinated SAM (PFDT) with CF<sub>3</sub> end groups drastically alters the surface energy and this SAM results in a highly hydrophobic surface, which causes a poor wetting of the rr-P3HT on the contacts. Therefore, we omitted data based on PFDT-modified transistors. However, the current–voltage characteristics of untreated transistors and transistors with HDT-modified gold electrodes are reliable and reproducible. The transfer characteristics of untreated and HDT-modified transistors with channel width of 10000 μm and channel lengths of 10, 15, 20, 30 and 40 μm were analysed with TLM and are plotted in Fig. 7. Since the HOMO level of rr-P3HT is located at 4.8 eV, an Ohmic contact is created with Au electrodes. For HDT treated Au contacts, the work function is changed to 4.0 eV. Consequently, an injection barrier for holes is expected. The mobility calculated from both transistor characteristics (untreated and HDT-treated) is  $(1\text{--}2) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at  $V_{\text{DS}} = -2 \text{ V}$  and high  $V_{\text{G}}$ , which is similar to the reported mobility for rr-P3HT.<sup>15,24,25</sup> Even though the mobility is an intrinsic materials parameter, which only depends on the temperature and charge carrier density,<sup>3,22</sup> analysis of the transfer and output characteristics with simplified models, such as the gradual channel approximation, will result in mobilities which deviate from the accepted values. Such models are founded on Ohmic contacts between the semiconductor and the electrodes, which is not always applicable. The contact resistance for the SAM-modified Au electrodes is one order of magnitude larger than that of a transistor with bare Au electrodes. Taking the analysis of Bürgi *et al.*<sup>6</sup> into account that the contact resistance is a combination of the resistances arising from the contact itself, the injection barrier and the bulk resistance at the interface, the difference in contact resistance can be attributed to the increase of the injection barrier due to the presence of the monolayer between the Au electrode and the semiconducting polymer. This is valid



**Fig. 7** Comparison of (a) contact resistance and (b) mobility *versus* gate voltage for the HDT-modified and untreated transistor with rr-P3HT as the semiconductor at  $V_{\text{DS}} = -2 \text{ V}$ .

if we assume that rr-P3HT adopts the same morphology at the interface with the Au electrode in the presence or absence of the HDT SAM.

### Conclusions

We demonstrate that self-assembled monolayers can modify the work function of gold from 4.0 eV to 5.6 eV for hexadecanethiol and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, respectively. Both SAMs on Au and their corresponding work functions are stable in time. Adjusting processing parameters like the concentration of the SAM in solution and the immersion time provides the opportunity to tune the work function. The alkanethiol-based SAMs on Au are shown to be thermally unstable when annealed above 60 °C. The SAM-modified Au electrodes are used in field-effect transistors to manipulate the injection of holes into polymeric semiconductors. Using the transfer line method (TLM), we have found the intrinsic mobility for MEH-PPV to be  $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and that for rr-P3HT to be  $(1\text{--}2) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

irrespective of the contacts. The contact resistances extracted from the TLM are at least one order of magnitude larger for the SAM-modified gold contacts with respect to the untreated Au electrodes. The transfer line method used here is more generally applicable than the gradual channel approximation, especially when non-Ohmic contacts are formed in organic field-effect transistors.

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